

ARMY RESEARCH LABORATORY



A Novel Manufacturing Processing Route for Forming High-Density Ceramic Armor Materials: Phase I - SBIR

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Abstract

The objective of the Phase I small business innovative research (SBIR) project was to demonstrate the feasibility of applying the Combustion Synthesis (CS)/Ceracon Consolidation Process for forming 10-cm-diameter, 2.5-cm-thick high-density titanium carbide (TiC) and titanium diboride (TiB₂) pieces. The Phase I project demonstrated for the first time the feasibility of CS initiation to form TiC and TiB₂ by using Ceracon's hot, granular media and their in-situ consolidation. The effects of applied pressure and pressure-transmitting media (PTM) temperature in controlling density, as well as thermal management issues to prevent cracking in applying the CS/Ceracon process to form TiC and TiB₂, have been identified. In-situ CS/Ceracon consolidation to densities exceeding 98% was demonstrated for fabricating 10-cm-diameter, 2.5-cm-thick TiC pieces. The CS/Ceracon-processed, high-density TiC specimen has a fine grain size, microhardness values exceeding 2,500 kg/mm², and compressive strength of 1.3 GPa. Due to the use of inexpensive conventional forging equipment and a low-cost grain for both initiating self-propagating high-temperature synthesis (SHS) and consolidation, this novel approach has the potential to be significantly more cost effective than currently used conventional hot pressing (HP) or hot isostatic pressing (HIPing) of TiC and TiB₂ powders. A set of recommendations for the technical approach to be followed in process upscaling in Phase II to fabricate larger size tiles of TiC material is provided.

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1. Objectives of the Phase I Small Business Innovative Research (SBIR) Program

The overall objective of this project was to determine the potential for economically mass producing low-porosity monolithic ceramic materials by Combustion Synthesis (CS)/Ceracon in the quantities and sizes required for ballistic applications.

In Phase I, a demonstration of the ability to apply the CS/Ceracon technique by fabricating 10-cm-diameter \times 2.5-cm-thick pieces of titanium carbide (TiC) at 95.57% of theoretical density and titanium diboride (TiB₂) at 98.57% of theoretical density was required. Microhardness values for these samples must be comparable with materials prepared by conventional hot-pressing (HP) methods.

2. Literature Search on CS/Dynamic Compaction TiC and TiB₂

Because of their attractive physical and mechanical properties, the boride and carbide of titanium have been the focus of attention in numerous investigations. Results have been reported in which the effects of the synthesis method, impurity contents, and densification processes on the final product have been examined. A brief summary of the important observations on selected publications follows. The summaries are classified under TiC and TiB₂ and include discussions on related composite materials.

2.1 TiC. TiC has been synthesized by combustion and consolidated by dynamic compaction [1, 2]. Samples with relative densities of 98% have been prepared. Their hardness was equal to or better than that obtained with conventionally prepared (commercial) materials. The hardness, however, showed a dependence on the stoichiometry of the TiC phase. The maximum hardness corresponded to a carbon/titanium (C/Ti) ratio of 1.0. However, at this ratio, the process of densification is not optimum and it was concluded that an ideal C/Ti ratio of 0.90–0.95 would give

the desired combination of ease of densification and high hardness. This observation is in contrast to that made by Miyamoto and Koizumi [3]. These authors synthesized and consolidated substoichiometric titanium carbide (TiC_x) in one step using what they refer to as "gas-pressure combustion sintering." Under a gas (argon [Ar]) pressure of 100 MPa, they were able to obtain fully dense TiC_x for $0.5 \leq x \leq 0.8$. Higher x value resulted in lower density products. The authors explain this in terms of having excess C, which inhibits densification in samples with $x > 0.8$. Another important parameter that influences the densification and the microstructure of TiC is the nature and level of impurities. Iron (Fe) impurities were found to degrade the properties of the carbide by segregating at the grain boundaries [1]. Other impurities in the reactants (Ti + C) can also play a role in the densification and microstructural development of the carbide [4, 5]. The major noncondensable impurities that were detected in the gas phase above the heated reactants include water, hydrogen, carbon monoxide, carbon dioxide (H_2O , H_2 , CO , CO_2), and hydrocarbons. Most of these types of impurities can be expelled by outgassing the reactant mixture at 500° C for several hours.

TiC has also been combustion synthesized and densified to 95% by the application of uniaxial pressure [6]. The application of 27.6 MPa pressure resulted in a TiC microstructure with a typical grain size of approximately 20 μm . In agreement with the observations of Niiler and co-workers [4, 5], the gases that evolved during combustion were found to contain a significant amount of H_2 . It was proposed that the presence of this gas is the result of an oxidation reaction of the metal (Ti) by H_2O or the evolution of dissolved H_2 from Ti. The latter interpretation is especially important in cases where the Ti is prepared from a hydride phase.

There are also reports of investigations on the synthesis and densification of TiC-containing composites. Composites such as TiC + alumina (Al_2O_3) are commercially important as cutting tools. TiC is added to Al_2O_3 to enhance toughness and limit undesirable grain growth. However, in the sintering of these composites, undesirable gas evolution leads to pore formation. Gas evolution in this case is the consequence of interaction between TiC and Al_2O_3 [7]. This composite has been investigated with respect to the feasibility of transformation toughening through the addition of zirconia (ZrO_2) [8]. In another investigation, it was found that a composite of Al_2O_3 +

30 weight-percent TiC can be sintered to a density > 97% at 1,950° C if the heating rate up to this temperature is > 200° C/min [9]. Presumably, higher heating rates diminish the extent of the interaction between Al₂O₃ and TiC. As indicated previously [7], such an interaction leads to the formation of gaseous products, which decrease the ultimate relative density of the composite.

2.2 TiB₂. As in the case of TiC, numerous investigations have been conducted on TiB₂. Using a gas pressure of 100 MPa, Miyamoto and Koizumi [3] succeeded in synthesizing and densifying TiB₂ up to a relative density of 99%. However, to attain density of this magnitude, the authors found it necessary to add 20 weight-percent excess Ti. It is interesting to note that the excess Ti appeared in the product as Ti₃B₄ and TiB. Thus the amount of TiB₂ is decreased by the addition of the excess Ti. TiB₂ has also been prepared by combining CS with shock consolidation [2, 10]. Relative densities in the range of 96–98% of theoretical have been achieved. In a manner similar to that used for TiC [6], TiB₂ has also been prepared and densified by the application of uniaxial pressure (82 atm) after the initiation of a combustion reaction between the elemental reactants [11]. The effect of Fe impurities on the sintering TiB₂ was investigated [12]. The presence of 0.5 weight-percent Fe leads to abnormal grain growth when the powder is sintered at 2,000° C in Ar. It was found, however, that the addition of boron carbide (B₄C) suppresses grain growth and a 95% dense TiB₂ can be prepared. The presence of oxygen as an impurity has a deleterious effect on the densification of TiB₂ by sintering. It has been proposed that oxygen impurities, presumably in the form of surface oxides, enhance surface diffusion [12], a process which does not contribute to densification but one which blunts the driving force for sintering [13]. Other investigations have also pointed out the detrimental effect of oxygen as an impurity. However, the interpretation of the role of oxygen differs. It has been suggested that oxygen enhances mass transport by an evaporation-condensation method through the species boron trioxide (B₂O₃) [14, 15]. Unfortunately, no attempt has been made to establish the level of oxygen impurity at which these deleterious effects occur.

As stated previously, the presence of Fe as an impurity in TiB₂ results in undesirable abnormal grain growth [12]. However, its presence as well as the presence of nickel (Ni) is seen as desirable when TiB₂ is to be hot pressed [15]. It was observed that when the content of Fe + Ni

< 0.1 weight-percent the material could only be pressed to a relative density of $\leq 88\%$ at $1,600^{\circ}\text{C}$, but when $\text{Fe} + \text{Ni} \geq 0.3$ weight-percent, the densification process was markedly enhanced. In this same study, it was also observed that the addition of C to TiB_2 diminished exaggerated grain growth. It is likely that this effect may be related to the role of C in reducing oxygen impurity and hence diminishing the nondensifying mass-transport processes of surface diffusion and evaporation condensation.

The densification of TiB_2 prepared from a solid-state reaction between titanium nitride (TiN) and amorphous boron (B) was also investigated [16]. Fine-grained ($2\text{--}3\text{ }\mu\text{m}$ in diameter) TiB_2 was prepared and densified to a relative density of 98% by HP under a pressure of 20 MPa at $1,800^{\circ}\text{C}$ for 5–60 min.

The preparation of composite materials containing TiB_2 has been investigated. In particular, reactions between Ti, aluminum (Al), and B to form a $\text{TiB}_2 + \text{Al}$ composite have been examined [17, 18]. In an earlier study [18], the addition of up to 20 weight-percent Al to the stoichiometric mixture of $\text{Ti} + 2\text{B}$ resulted in TiB_2 as a product with no evidence of free Al. In contrast, the more recent study [17] showed that Al is present in the product. It should be noted that the earlier study was conducted in vacuum, while the latter work was carried out in an atmosphere of Ar. It is therefore likely that under vacuum conditions, excessive evaporation of Al lead to its absence in the product. Related to this study is an investigation by Halverson et al. [19] on the formation of $\text{TiB}_2/\text{B}_4\text{C}$ composites. The goal of this study was to synthesize, by combustion, composites with a varying ratio of $\text{B}_4\text{C}/\text{TiB}_2$, which would subsequently be infiltrated by Al metal.

3. Background on the Ceracon Process

The Ceracon process is a patented [20], low-cost powder metallurgy process for achieving near-net shape, full-density parts. It is a simple consolidation technique that uses conventional powder metallurgy equipment and setup. The Ceracon process is a quasi-isostatic, hot consolidation technique that uses a ceramic particulate material as pressure-transmitting medium (PTM) instead of

a gas medium as used in hot isostatic pressing (HIPing). Pressures up to 1.24 GPa can be used, and materials can be processed at unlimited upper temperatures. The process consists of four steps as detailed in Figure 1: (1) fabrication of green preform, (2) part heating and grain heating and transfer to the Ceracon die, (3) consolidation, and (4) part removal and grain recycling.

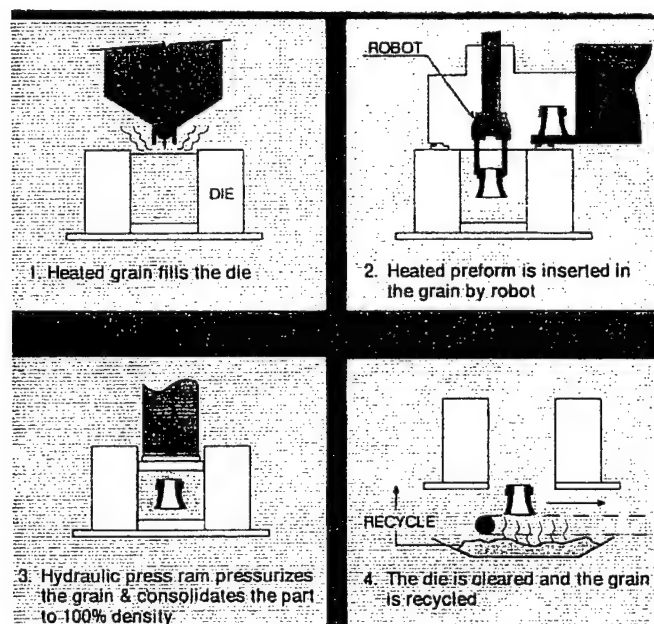


Figure 1. The Ceracon Process.

The low temperature coupled with short time consolidation capabilities of the quasi-isostatic, hot-consolidation, high-pressure process has been applied to a broad range of material systems. The various systems processed include Al 6061 and 2124, tool steel, 46XX steel, Al-Fe-V-Si, TiAl, Cu, Nd-Fe-B supermagnets, superalloys, Al-SiC MMCs, WC-Co to Fe, Nb Alloys, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors.

The idea of using PTM to initiate self-propagating high-temperature synthesis (SHS) reaction and subsequently superimposing pressure on the part in situ had not been explored before. This approach,

if successful, will have significant advantages over thermite-induced SHS consolidation approaches, because:

- technology capability for consolidating parts from conventional materials, such as steel, up to 17.8 cm diameter \times 61 cm long, has already been demonstrated;
- thermal management of the specimen during and after processing is readily possible because of immediate specimen access after consolidation is completed; and
- the equipment is easy to set up and operate without the elaborate features required from other processes, such as HIPing, HP, and CS/explosive consolidation.

4. CS/Ceracon Processing of TiC and TiB₂ (Process Development Using Subscale Specimens)

The work on applying the in-situ CS/Ceracon processing was carried out initially using subscale 2.5-cm-diameter, 0.64–1.21-cm-thick specimens. The details on selection and procurement of elemental powders, powder blending, green preform fabrication, evaluation of critical Ceracon process parameters for achieving high density, and identification of thermal management issues to prevent cracking and specimen containment are summarized below along with the conclusions regarding upscaling to fabricate 10-cm-diameter, 2.5-cm-thick specimens.

4.1 Identification and Procurement of Elemental Powders. Significant prior work has been carried out leading to identification of the desirable characteristics of elemental powders used in CS by Niiler, Kecskes, and Kottke [2], Meyers et al. [21], and Holt and Munir [6]. This information was used in selecting the appropriate elemental Ti, C, B, and TiB₂ (diluent). Ultrafine MicroTi (<20 μ m) Ti was procured from Micron Metals Inc., Salt Lake City, UT. This particle size and this particular Ti powder fabrication technique has been identified by a U.S. Army Ballistic Research Laboratory

(BRL) [22] study to be suitable for CS. The analysis of Ti powder provided by the manufacturer is shown in Table 1.

Table 1. Chemical Analysis of Ti Powder

Material Description: Titanium Metal Powder, Dry Specification: -20- μ m 'Micro Ti'	
Ti, Minimum	99.00% Minimum Balance
O	0.32% Maximum
N	0.03% Maximum
C	0.05% Maximum
Fe	0.08% Maximum
Si	0.05% Maximum
Al	0.01% Maximum
Chlorides	0.15% Maximum
Packed Density	1.72 g/ml
Surface Area	1.60 m ² /g

Two sources were investigated for graphite (C) powder: CERAC Inc. and Consolidated Astronautics, Inc. Based on the superior combustion characteristics of Consolidated Astronautics' powder, all processing and upscaling studies exclusively used the Consolidated Astronautics' graphite powder. Analysis of this powder is provided in Table 2. The B powder and diluent TiB₂ was procured from CERAC and Union Carbide, respectively (see Table 2).

4.2 Powder Blending. Both dry blending [21] and wet blending [21] have been successfully used for obtaining a homogeneous blend of Ti and C as well as Ti and B. In view of the dust-free blending feasibility in a wet medium, this approach was selected for all blending work. A rotary jar mill was used for blending processing. Elemental powders, ethanol, and the milling media (WC-Co nibs) were mixed in the volumetric ratio of 25%:50%:25%. The ball milling operation was carried out for a 2-hr period to achieve a blend having excellent homogeneity. The ethanol was removed by drying the blended slurry in an oven. After ensuring complete evaporation of ethanol, the powder blend was used in subsequent green preform fabrication operation.

Table 2. Chemical Analysis of B and Graphite Powders

Material Description:	Graphite, C 2 μm	Metal, B Typ. 1 μm or less
Purity	99.9%	99.9+ %
Size (Fisher)	0.54 μm	0.21 μm
Spectrographic Analysis (%)	Al 0.002 Ca 0.01 Fe 0.005 Mg 0.001 Si 0.01 Sr 0.002 Ti 0.01	Al <0.001 Ca <0.001 Cu 0.001 Fe <0.001
X-ray Diffraction (XRD) Analysis	—	B matches PDF # 31-206 tetragonal

4.3 Green Preform Fabrication. There are principally two processes available for fabricating preforms: cold pressing (CP) and cold isostatic pressing (CIPing). Ceracon has capabilities for CP (up to 10 cm diameter) and CIPing (17.8-cm-diameter, 61-cm-long billets have been demonstrated). Both processes were evaluated for the fabrication of disk-shaped specimens required in this program. It was found that both processes work suitably well, and no difference in the combustion characteristics of the compacts fabricated by either process is noted if the preforms had identical green densities to start with. The CP was used to fabricate all specimens in the process development study, while CIPing was perfectly suited and used for the larger 10-cm-diameter, 2.5-cm-thick specimens.

4.4 CS/Ceracon Consolidation.

4.4.1 TiC. The following issues were considered to be critical to meeting the goals of BRL specifications for TiC:

- Complete conversion of Ti + C to TiC.

- Densification to a minimum of 95.57%.
- Achieving crack-free specimens.

The CS/Ceracon process evaluation involved test matrix experiments to clearly identify the role of:

- PTM characteristics.
- PTM temperature required to initiate CS.
- The amount of pressure required to densify and the precise time and pulse duration of pressure application.
- Thermal management issues to address specimen crack prevention.

The details of each of these parameters and processing issues will be addressed in the following:

4.4.1.1 PTM Characteristics. The core of the Ceracon process is its use of solid particulates of carbonaceous and ceramic PTM to affect densification of a part. The use of a variety of PTMs is protected by several U.S. Patents issued to Ceracon. Using hot PTM to initiate CS heretofore has not been reported and is considered patentable. The key characteristics relevant to CS is the identification of the presence of any deleterious reaction between the PTM and compact undergoing CS reaction. In this project, a carbonaceous PTM known as 9400 and a mixture PTM consisting of a blended mixture of 9400 + Al_2O_3 were evaluated (Table 3).

The 9400 PTM was found to be nonreacting with the CSed TiC material; whereas the 9400 + Al_2O_3 mixture was found to have some melting and surface bonding of Al_2O_3 to the TiC. However,

Table 3. CS/Ceracon Test Matrix Experiments on Subscale Specimens

SN	PTM Temp (° C)	Delta Times in Seconds		Dwell at Full Pressure (s)	Variable Modified		Density Recorded (%)	Specimen Composition
		Sample Insert - SHS Observed	SHS Until Full Pressure		Time SHS Observed Until Pressure Applied	PTM Type		
900	1,200	30	3	60	Pressure applied when SHS is observed	Al/9400	95.0	TiC
901	1,200	43	10	60	Same as above	Al/9400	95.0	TiC
902	1,200	—	4.7	30	Same as above	9400	97.0	TiC
904	1,200	30	5.4	60	Same as above	9400	98.0	TiC
CERAC Carbon	1,200	38	4	60	Same as above	Al/9400	95.7	TiC
905	1,200	30	5.8	60	Same as above	9400	97.3	TiC
906	1,200	32	6	60	Pressure applied 3 s after SHS is observed	Al/9400	95.0	TiC
910	1,200	36.6	4.5	60	Pressure applied 1 s after SHS is observed	Al/9400	96.0	TiC
951	1,200	44	4	60	Pressure applied when SHS is observed	Al/9400	82.4	Ti, B, and TiB ₂
952	1,200	50	4	60	Same as above; punch inserted .318-cm into die prior to SHS	Al/9400	84.6	Ti, B, and TiB ₂
953	1,200	50	4	60	Same as above; punch inserted .635-cm into die prior to SHS	Al/9400	83.7	Ti, B, and TiB ₂

NOTE: Unless otherwise noted, all samples had the following common parameters: Consolidation at 1.24 GPa, sample weight for both materials: 10 g; TiC preform size = 2.56 cm diameter × 0.64 cm thick; TiB₂ preform size = 2.578 cm diameter × 0.952 cm thick; die cavity size = 6.35 cm diameter × 3.81 cm deep.

this surface bond could be easily removed. In view of the ease of flow and part removal, 9400 was selected and used for the majority of the work.

4.4.1.2 PTM Temperature. The PTM temperature required to initiate CS reaction was investigated. The combustion initiation temperature for TiC was measured from differential thermal analysis (DTA) experiments as a function of heating rate. In the range of heating rates investigated, the initiation temperature was constant at 1,550° C (Figure 2). PTM temperatures of 1,600° C,

1,400° C, and 1,200° C were used to monitor combustion initiation. It was possible to initiate combustion at a temperature of PTM as low as 1,200° C. The initiation of reaction was visible by "Fireworks" resulting from the expulsion of small quantities of fiery grain from the die.

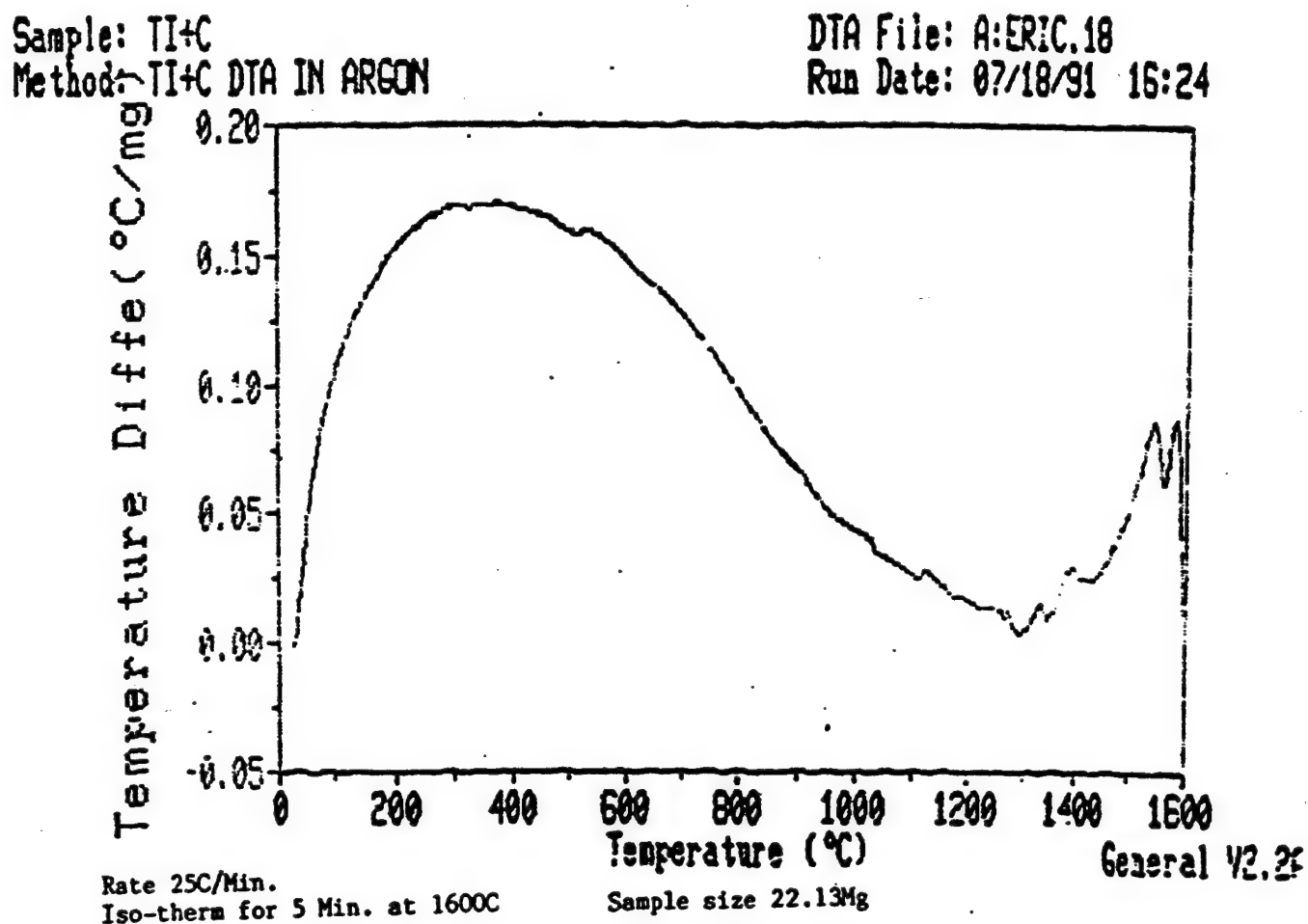


Figure 2. The Study of CS in a Differential Thermal Analyzer.

The onset of combustion was consistent and reliable from one run to another. The time from initial contact of the hot PTM to the green preform to combustion initiation was longer, ~4.30 min for larger size specimens and 60 s for smaller specimens.

PTM initiated CS of TiC was carried out without applying any pressure on the PTM. Resultant specimens were characterized for conversion to TiC using XRD density of the specimens. It was noted that complete conversion to TiC was achieved using Consolidated Astronautics' graphite powder, and a density of 75% of theoretical was achieved with expansion in specimen dimension noticed, as is typical of specimens undergoing combustion reaction.

4.4.2 The Effect of Applied Pressure on Densification and Coordination of Its Timing. The Ceracon process used a pressure of up to 0.69 GPa in a die cavity size of 20 cm diameter and 1.38 GPa in a die cavity size of 6.35 cm diameter. In applying pressure in situ to a CS reaction to form TiC, several experiments were carried out involving (Table 4):

- (1) Application of pressure on the specimen prior to combustion initiation by hot grain and holding it through combustion. This approach tended to cool the grain prematurely and resulted in noninitiation of combustion or a partial combustion reaction.
- (2) Application of pressure upon observation of combustion and slowly ramp up the magnitude of pressure. The densities achieved were only 85% of theoretical for TiC because the pressure pulse did not superimpose on the material when specimen was at the highest temperature.
- (3) Delay application of pressure after initiation of combustion for a few seconds, then apply pressure. This worked well leading to full conversion to TiC and high densities achieved.
- (4) Delay application of pressure after the observation of combustion for a few seconds but apply rapid pressurization. This worked the best giving a combination of highest densities (>95%) and full conversion to TiC.

The mode described in (1) or (4) was used in a majority of the thermal management experiments and in upscaled fabrication of 10-cm-diameter, 2.5-cm-thick specimen fabrication.

Table 4. CS/Ceracon Experiments to Fabricate TiC

SN	PTM Temperature (° C)	Delta Times in Seconds		Variable Modified	PTM Type	Density Recorded
		Sample Insert - SHS Observed	SHS Until Full Pressure			
Unless otherwise noted, all samples had the following common parameters: Consolidated at 0.48 GPa; die cavity size - 6.35 cm diameter × 12.7 cm deep.						
2	1,200	No SHS	—	Cold sample placed in heated graphite vessel; same as PTM temperature.	9400	—
3	1,200	No SHS	—	Same as above added: TiB ₂ cap on top of sample.	9400	—
933	1,400	1 min	No pressure applied	Same as above added: higher heat for PTM and vessel, 1,400° C.	9400	—
936	1,400	1 min	No pressure applied	Same as above.	9400	—
Unless otherwise noted, all samples had the following common parameters: Consolidated at 0.48 GPa; die cavity size - 8.57 cm diameter × 12.7 cm deep.						
939	1,200	1 min	—	Same as above; material from newer batch; sample appears to have exploded at SHS.	9400	96.0
931	1,400	1.6 min	—	Same as above added; 9400 PTM.	9400	97.0
Unless otherwise noted, all samples had the following common parameters: Consolidated at 0.48 GPa; die cavity size - 10.1 cm diameter × 12.7 cm deep; media heated to 1,200° C.						
942	1,200	50 s	10 s	40.6-cm diameter × 1.78-cm sample with ring; sample at top edge of ring; appears that top of sample is moved out of ring at SHS.	9400	100 ^a
943	1,200	3.5 min	10 s	Same as above with sample in middle; appears to barely have sufficient heat for SHS to occur.	9400	103.0 ^a
944	1,200	50–60 s	10 s	Same as first; same post-Ceracon condition.	9400	100.0 ^a

^a Analysis showed Fe contamination leading to high density.

The high-density TiC specimens were found to have a network of surface cracks, similar in appearance to that reported by Meyers et al. [21]. The cracks originate from thermal shock experienced by the specimens due to rapid cooling of the specimen after densification and due to the differential cooling rate between the surface and interior. Another problem noted during

consolidation was the shifting of the specimen into two layers, which led to specimen distortion and differential consolidation of the specimens.

4.4.3 TiB₂. The following issues were considered to be critical to meeting the specifications set for CS/Ceracon-processed TiB₂:

- Density of at least 98.5%.
- Conversion to TiB₂.
- Achieving crack-free specimens.

Most of the process parameters and issues discussed previously for TiC are common to TiB₂; however, there are some differences that are highlighted in the following discussion.

4.4.3.1 PTM Characteristics. The use of carbon-based media for CS/Ceracon of Ti + B to form TiB₂ was of concern because of the potential for reaction between carbonaceous media and elemental Ti to form TiC in addition to TiB₂. However, free energy calculations of delta G vs. temperature show that TiB₂ has significantly higher free energy of formation; hence, it should not be a problem using carbon-based PTM (Figure 3).

4.4.3.2 PTM Temperature. The PTM temperature of 1,200° C was adequate to initiate combustion readily; however, in carrying out the reaction of pure Ti with B, the reaction process was significantly more energetic than the reaction of Ti and C leading to specimen disintegration. This problem led to the identification of need for use of diluent TiB₂. Later CS/Ceracon experiments were carried out with the addition of 22.5 weight-percent of TiB₂, as suggested from the work of Meyers et al. [21]. However, the addition of diluent led to obtaining lower density values of 85%.

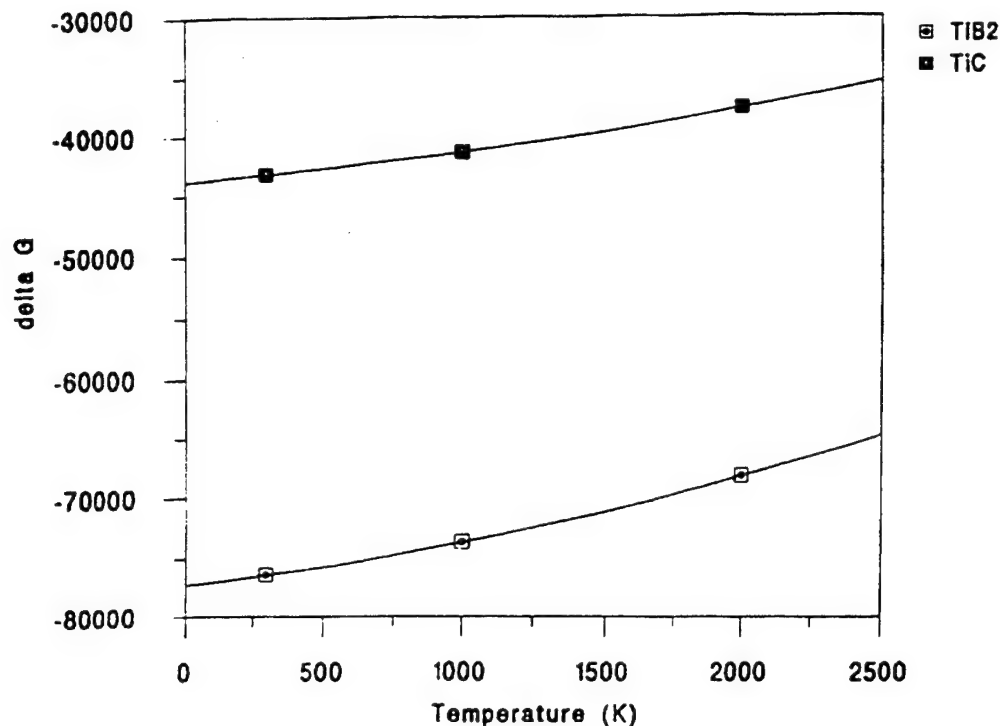


Figure 3. Delta G vs. Temperature for TiB₂ and TiC.

The microstructure of the TiB₂ specimen obtained by CS/Ceracon is shown in Figure 4. The fine grain size present shows the process' capability to achieve densification without grain growth.

Due to the more explosive reaction involved in the formation of the TiB₂ leading to safety problems, and due to the high cost of B, we decided to dedicate all the remaining effort in Phase 1 to demonstrating the fabrication 4-in-diameter × 1-in-thick TiC specimens.

5. Thermal Management Issues to Prevent Crack Formation and Specimen Containment

In their earlier work on high-speed forging coupled to CS of TiC and TiB₂, Meyers et al. [21] had identified the crack problems and crack origins. Niiler, Kecskes, and Kottke [2] have also addressed similar issues in the CS/dynamic compaction of TiC and TiB₂. These studies have identified that containment of the specimen during CS by using a combination of grafoil and steel concentric outer rings prevented specimen displacement, and immediate slow cooling of the specimen after

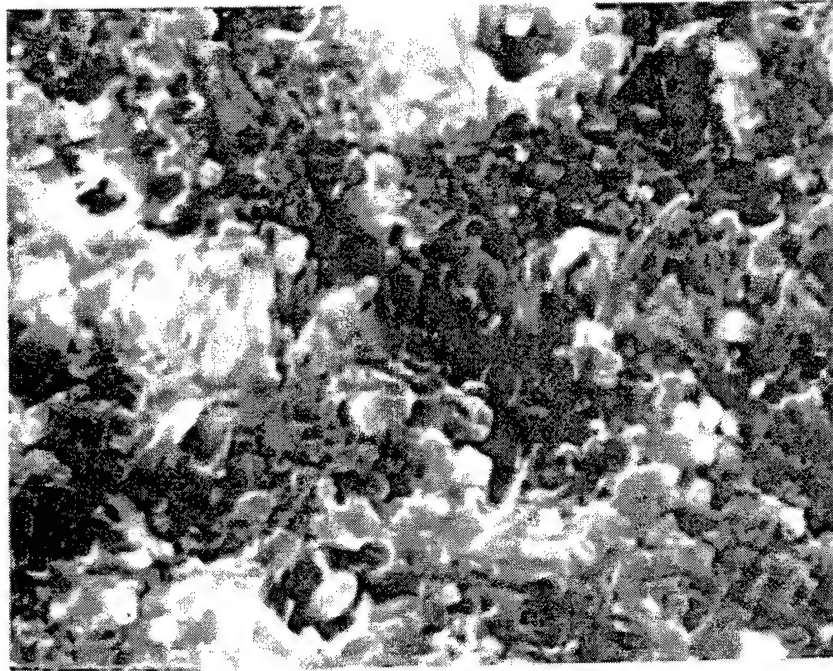


Figure 4. Scanning Electron Microscope (SEM) Micrograph of Surface of TiB_2 at 1,000 \times .

CS/dynamic compaction in a furnace for an extended period solved thermal cracking problems. These findings were incorporated in this work initially, but because of the different material processing environment present in the Ceracon die vs. hot forging or explosive consolidation, a new type specimen confinement system was developed and found to be more suitable.

Specifically, the steel ring/graphite or graphite confinement ring works well for consolidation, but the high temperatures resulting from CS cause the steel to melt and mix with consolidated TiC (Table 4), leading to a significant amount of Fe contamination in the TiC, which is unacceptable. In view of this problem, we have removed the steel ring and designed a one-piece, all-graphite confinement ring.

To overcome the thermal shock problem, a number of techniques were evaluated, including in situ cooling of a CS/Ceracon-processed part in the die inside the PTM grain, cooling the part outside the die in a vessel containing an insulating blanket, and cooling in a furnace. While most cracks were eliminated, a surface crack was still present, which is most likely due to differential temperatures (as

identified by grain size difference) between the interior and exterior of the part. This problem can be solved by instantaneous removal of a specimen encased in hot PTM grain and placing it in a furnace and cooling slowly over an extended period of time.

5.1 CS/Ceracon Processing of 10.1-cm-Diameter \times 2.5-cm-Thick TiC. The powder blending, green preform fabrication, and CS/Ceracon processing parameters were upscaled to the fabrication of larger TiC specimens and no problems were noted. The final processing parameters used in these experiments are listed in Table 5.

Table 5. Processing Parameters for CS/Ceracon of TiC (10.1 cm Diameter \times 2.5 cm Thickness)

PTM:	9400
PTM Temperature:	1,200° C
Time to Ignite:	~4 min 30 s
Thermal Management:	Graphite Ring
Pressure:	0.48 GPa

CIPing of 4 kg of blended Ti and C powder was carried out to fabricate a cylindrical green preform with a 15.2 cm length and 10.1 cm diameter (Figure 5). Three discs were cut from this preform for use in CS/Ceracon processing. The larger 2,500-ton Ceracon press was used in these experiments (Figure 6).

The original containment fixture consisting of a grafoil inner ring followed by steel was abandoned in favor of an all-graphite ring as shown in Figure 7. This approach was taken because melting of the ring lead to contamination of TiC by Fe.

The CS/Ceracon experiments were then carried out using the following procedure. The graphite ring and PTM were separately heated to a temperature of 1,200° C. Approximately half the amount of grain was transferred to the die initially at 1,200° C, and a hot graphite ring at the same temperature was placed in the semifilled die. The green preform was lowered to approximately the middle of the ring to allow for anticipated expansion during CS. Approximately 5 min from the time

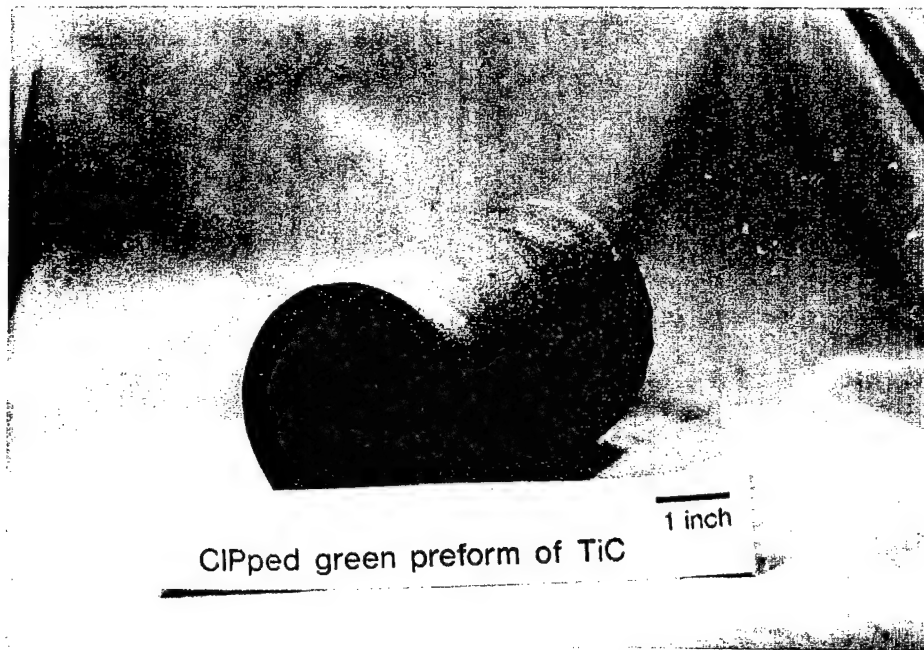


Figure 5. CIPed Green Preform of TiC.



Figure 6. Ceracon's 2,500-Ton Press.

- PROCESS STEPS:
 1) FIRST LOAD
 PTM, 1200°C.
 2) PLACE CONTAINMENT
 RING, 1200°C.
 3) PLACE PREFORM
 AMBIENT.
 4) SECOND LOAD
 PTM, 1200°C.
 5) WAIT FOR SHS.
 6) APPLY PRESSURE
 AFTER SHS.

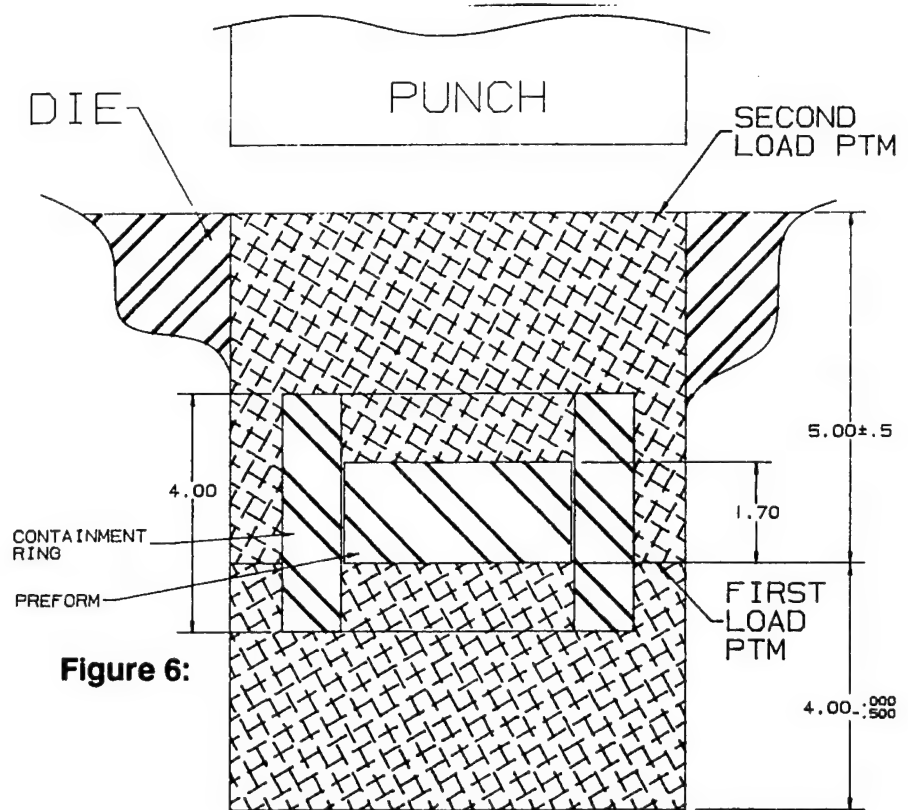


Figure 6:

Figure 7. Schematic of an All-Graphite Ring.

the ring was placed in the die, the initiation of CS reaction was visible by “fireworks” resulting from some expulsion of red hot, flaming PTM from the die. At this point, the pressure initiation cycle was initiated and a pressure of approximately 0.48 GPa was applied on the specimen that has just undergone SHS. Several 10.1-cm-diameter \times 2.5-cm-thick specimens of TiC were fabricated in this manner (Figure 8).

5.2 Post CS/Ceracon Thermal Management. After the consolidation cycle was completed, pressure was removed from the top of the specimen by withdrawing the punch, and the specimen was allowed to cool in the die amidst the hot PTM grain for a few minutes. After this time, the specimen was removed from the PTM grain and immediately transported to a vessel containing additional hot PTM grain surrounded by an insulating blanket of kaowool. The specimen that was cooled in this

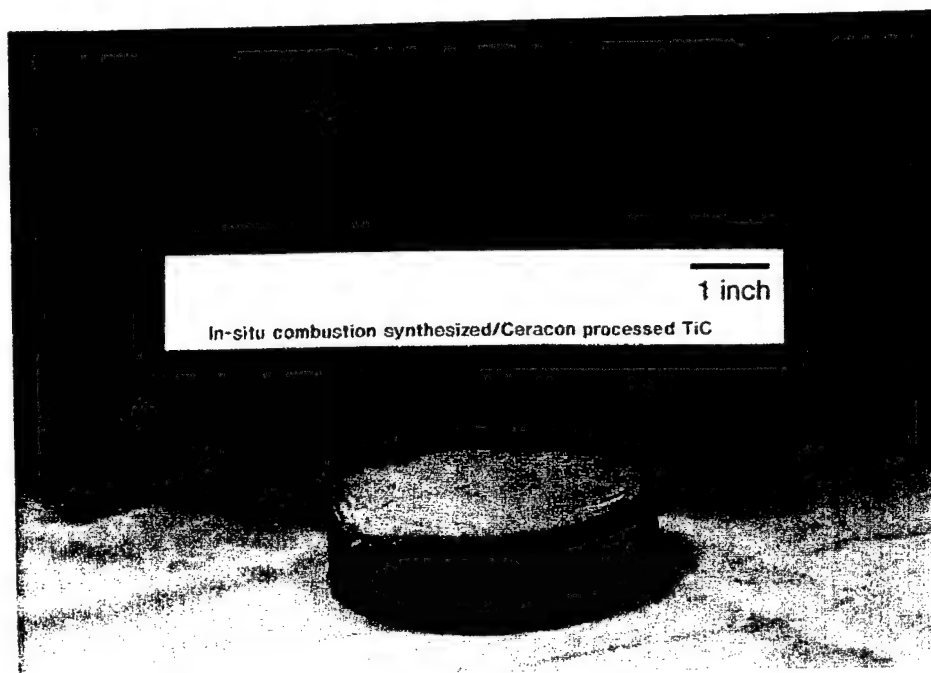


Figure 8. In-Situ CS/Ceracon-Processed TiC.

manner remained intact in one piece with only few surface cracks. Alternatively, specimens were also transported to a furnace where they were allowed to cool slowly prior to removal. The densities of these specimens were measured to be consistently exceeding 95.57%. The specimen was then characterized and tested. Using a diamond saw, the specimen was cut into small cubes for compression testing, microstructural characterization, and measurement of microhardness, toughness, and Young's modulus.

These upscaled TiC fabrication experiments clearly demonstrated the feasibility of fabricating an integral piece of specified density. These experiments also illustrated the importance of slow and uniform cooling of the interior and exterior of the specimen after CS/Ceracon to prevent crack formation.

6. Characterization of a 10.1-cm-Diameter \times 2.5-cm-Thick TiC Specimen

The characterization and testing of 10.1-cm-diameter TiC specimens was carried out by Professor Marc Meyers' group at the University of California, San Diego.

6.1 Specimen Preparation. The specimen was sectioned using a diamond saw. Specimens for mechanical testing were made by grinding cubes with dimensions of $6 \times 6 \times 6$ mm. The parallelism between opposite faces was very critical in order to ensure reliable mechanical properties; the precision in machining was kept to 2/10,000 (0.0005 mm). Larger variations in thickness could significantly affect the mechanical strength. The cubical mechanical specimens were tested in compression, at a nominal strain rate of 10^{-4} /s. Molybdenum disulfide was used as lubrication between the specimen and the machine platens (tungsten carbide). A screw-driven Instron with a 20,000-lb capacity was used for testing.

Vickers microindentation hardness measurements were made on a polished surface using a load of 300 gf, in a Leco microhardness testing machine. Specimen preparation for optical microscopy consisted of diamond polishing down to 0.25 μ m. The specimen was etched for metallographic observation in a solution of two parts nitric acid, one part hydrofluoric acid, and one part acetic acid. Metallography was carried out in a Nikon metallograph. For SEM, a unit from Cambridge Instruments was used.

6.2 Results and Discussion. Figure 9 shows the cross section of the TiC disk. The material has a very well consolidated appearance; the presence of some cracks in some sections is clear. The cracks are similar to the ones observed after the SHS/dynamic compaction process [21, 23]. They are most probably produced by thermal stresses during the cooling of the specimen.

The microindentation hardness was measured along the thickness of the specimens, and the results are shown in Figure 10. The values are found to fluctuate above 2,000 kg/mm².

The compressive strength of compacts was determined, and the results of three experiments are shown in Table 6. The compressive strength varied between 1.262 and 1.609 GPa. This value is also consistent with values obtained by Meyers et al. [21], and LaSalvia, Meyer, and Meyers [23]. Young's modulus in compression was measured indirectly through the deflection of the specimens as required in the recorder (correcting for machine stiffness). The values of Young's modulus, shown in Table 6, are lower than those for fully compacted and flawless material. Young's modulus of the



Figure 9. Optical Micrographs of Sectioned Specimens. Macrocracks Can Be Seen Transversing the Thickness.

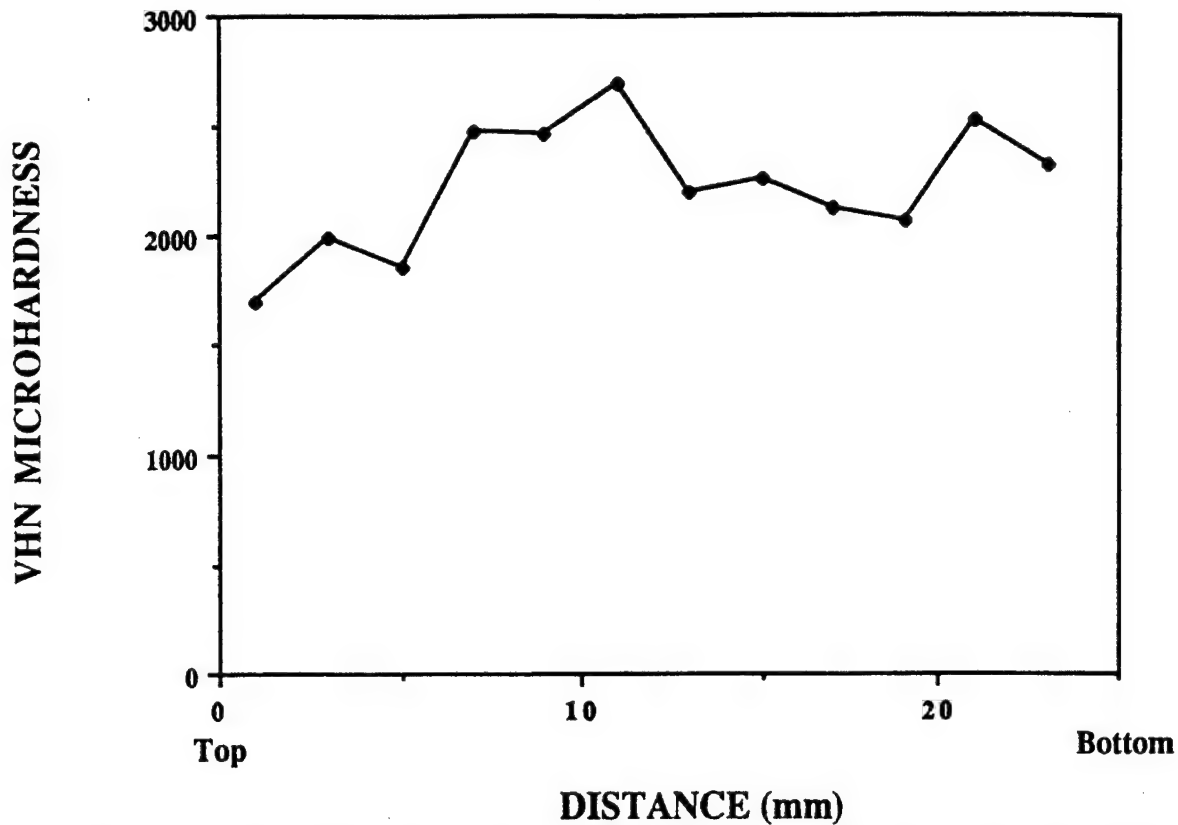


Figure 10. Microindentation Hardness Measurements Along the Thickness of the Specimen.

Table 6. Compressive Strength and Young's Modulus of TiC

Specimen	Compressive Strength (GPa)	Young's Modulus (GPa)
1	1.260	164.2
2	1.370	98.0
3	1.610	120.0

latter material varies between 400 and 500 GPa, while the values measured fluctuate from 98 to 164 GPa. The differences are possibly partially due to the presence of the lubricant between the platens. Nevertheless, it is known that cracks and pores affect Young's modulus. Hoke et al. [24] have introduced corrections into the values of Young's modulus due to these flaws and are able to explain the differences.

A preliminary fracture toughness measurement was made by measuring cracks remaining from the indentation produced by a microhardness tester. This technique was developed by Evans and

Charles [25] and has been successfully used by many investigators and correlated with fracture toughness measurements made by other techniques [25, 26, 27]. The indentation diagonals, a , are equal to 0.02 mm when a Vickers indenter with a load, P , of 500 gf was used. The average crack size, C , was 27 μ m. The fracture toughness, K_{Ic} , is obtained from the equation below:

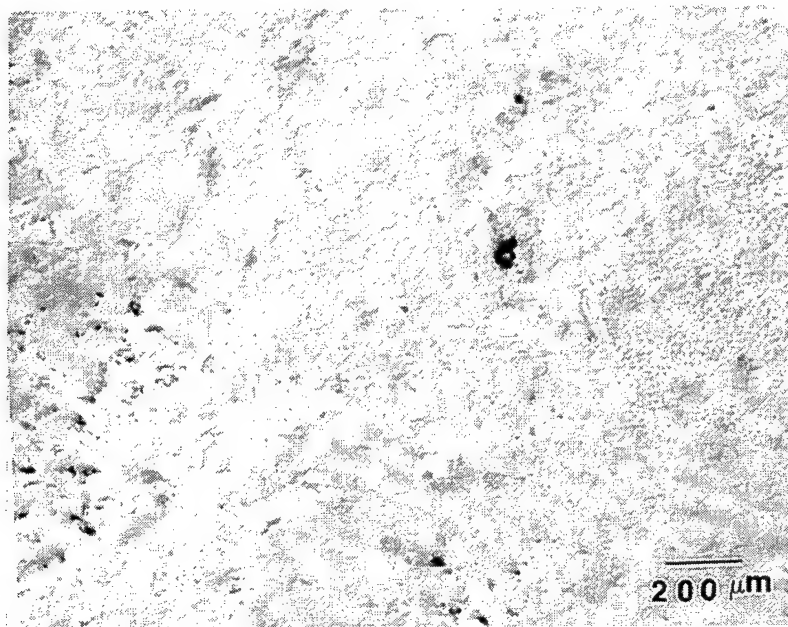
$$\begin{aligned} K_{Ic} &= 0.16 H a^2 C^{-3/2} \\ &= 0.16 \times 0.47 P C^{-3/2} \\ K_{Ic} &= 1.7 \text{ MPa m}^{1/2} \end{aligned}$$

The value obtained for K_{Ic} is characteristic of a well-bonded ceramic. Higher magnification optical micrographs reveal the grain structure in more detail. It is equiaxed and is shown in Figure 11.

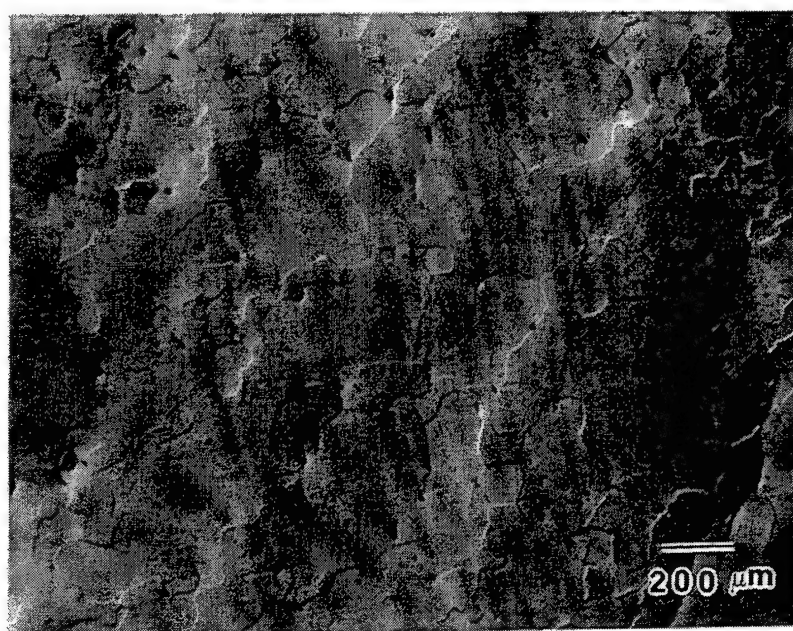
SEM of the specimens fractured in the compression test is shown in Figure 12. The fracture is clearly transcrystalline, and one sees the cleavage steps very well. Figure 13 also shows an area in which fracture has some intercrystalline features. This primarily transcrystalline fracture is a good evidence for good bonding between the grains and clean, impurity-free grain boundaries.

7. Accomplishments

- (1) The general overall objective of this project of demonstrating a process with potential for economically mass producing low-porosity monolithic ceramic materials by CS/Ceracon in the quantities and sizes required for ballistic applications was accomplished.
- (2) The specific overall objective of the ability to apply the CS/Ceracon process to fabricate 10.1-cm-diameter \times 2.5-cm-thick pieces of TiC at 95.57% of theoretical density has been met. The microhardness values of these samples are comparable to those obtained by conventional HP.

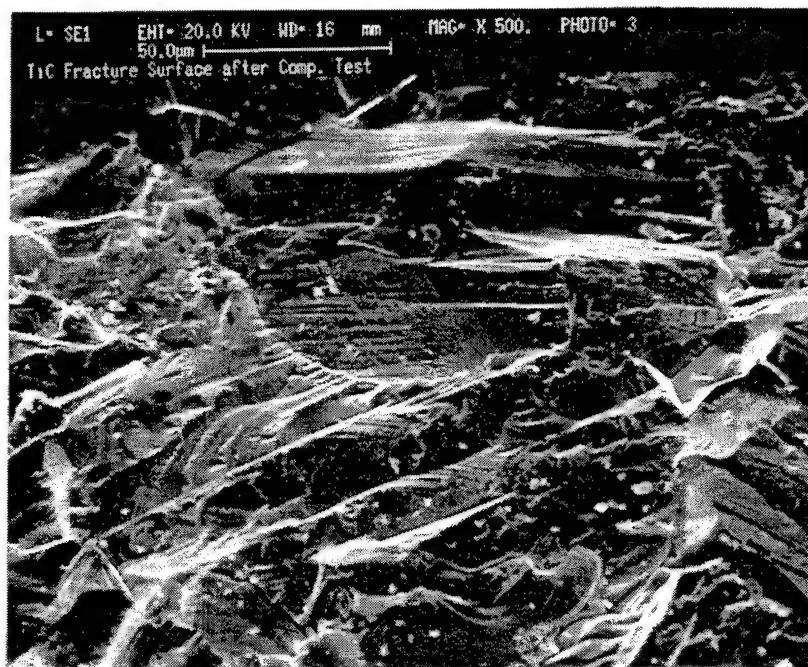


(a)

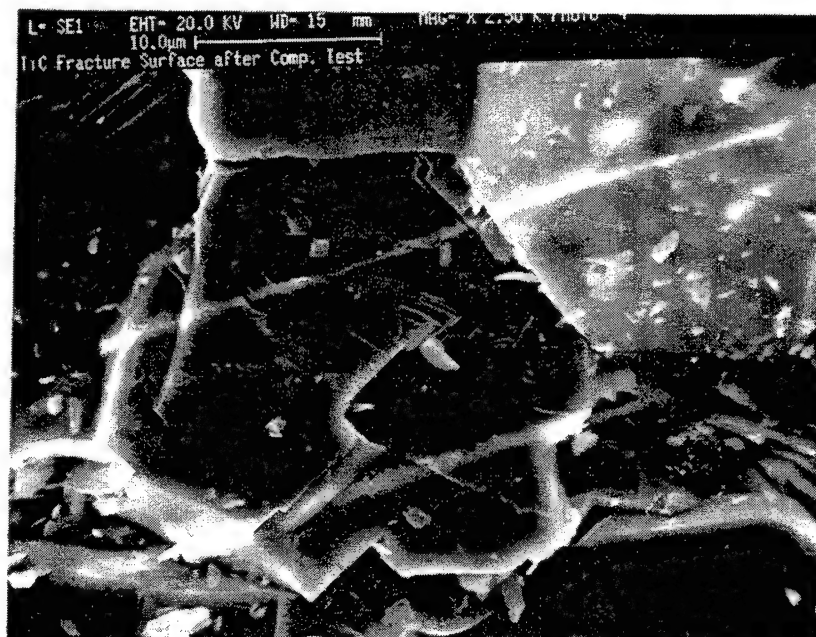


(b)

Figure 11. Optical Micrographs of Polished and Etched Sections of Specimen: (a) Small Grain-Sized Region Close to External Surface; (b) Large Grain-Sized Region Close to Center.



(a)



(b)

Figure 12. Fractographs of TiC Obtained by SEM Showing Primarily Transgranular Fracture: (a) Magnification of 500x; (b) Magnification of 1000x.

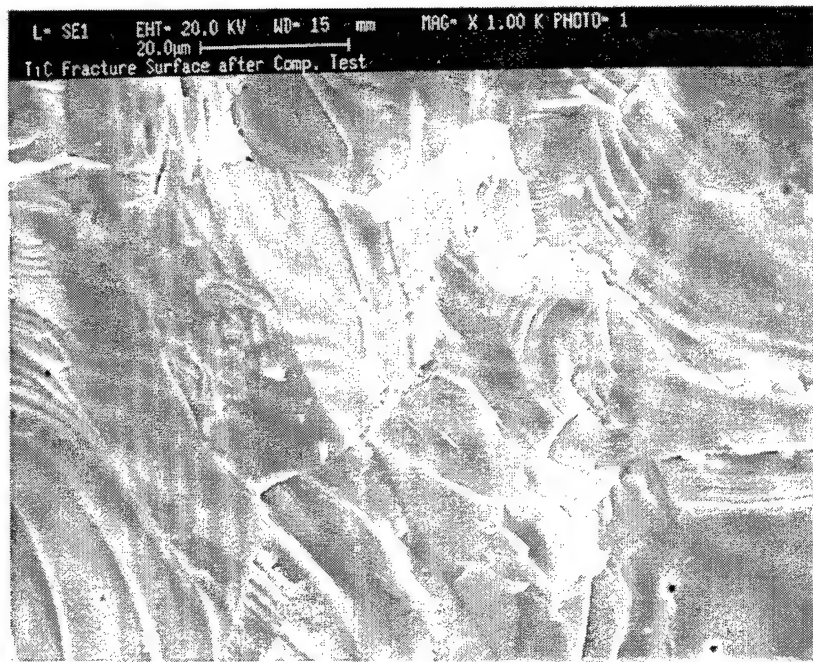


Figure 13. Fractographs of TiC Showing Partial Intergranular Fracture.

- (3) The characterization requirements set by the Contracting Officer's Technical Representative (COTR) has been met, including measurement of microhardness, compressive strength, Young's modulus, fracture toughness, density, XRD pattern, and SEM of surface and fracture surfaces. The required microhardness value of 25 GPa for TiC was met.

8. Conclusions

The use of the CS/Ceracon process is ideally suited for the fabrication of low-porosity monolithic ceramic materials, especially TiC. Complete conversion from $\text{Ti} + \text{C} \rightarrow \text{TiC}$ is feasible, and required densities of 95.57% can be readily achieved. The microstructure consists of larger grains toward the center of the specimen and smaller grains at the edge, most likely due to the need for better control in uniformly cooling the specimens. This may also be the reason for the presence of surface cracks in the specimen.

The economics of this process also looks very promising for the Army to fabricate TiC armor tiles for ballistic protection. This projection is based on the following reasons. When TiC powder is hot

pressed at very high temperatures (2,500° C), it requires a significant consumption of energy. The energy consumption CS/Ceracon process is much lower due to the use of temperatures of only 1,200° C. The PTM is inexpensive (\$0.50/lb), recyclable, and environmentally acceptable. The Ceracon processing technology and preform fabrication technology are already developed for conventional material systems, and thus technical expertise on the processing technology is readily available to this project.

9. Recommendations

The CS/Ceracon process, having met most of BRL goals for TiC in the Phase I program, is ready for Phase II process development and upscaling. In Phase II, it is recommended that work should focus on fabricating and demonstrating prototype fabrication of 100 pieces of 15-cm × 15-cm × 2.5-cm-thick tiles of TiC by the CS/Ceracon process. The work should initially address improving thermal management to produce totally crack-free specimens, including an understanding of heat transfer characteristics in the Ceracon environment followed by evaluation of cost issues in manufacturing TiC tiles. Extensive material characterization and testing of relevant microstructural and mechanical properties relevant to ballistic performance should also be carried out.

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13. ABSTRACT (Maximum 200 words) The objective of the Phase I small business innovative research (SBIR) project was to demonstrate the feasibility of applying the Combustion Synthesis (CS)/Ceracon Consolidation Process for forming 10-cm-diameter, 2.5-cm-thick high-density titanium carbide (TiC) and titanium diboride (TiB ₂) pieces. The Phase I project demonstrated for the first time the feasibility of CS initiation to form TiC and TiB ₂ by using Ceracon's hot, granular media and their in-situ consolidation. The effects of applied pressure and pressure-transmitting media (PTM) temperature in controlling density, as well as thermal management issues to prevent cracking in applying the CS/Ceracon process to form TiC and TiB ₂ , have been identified. In-situ CS/Ceracon consolidation to densities exceeding 98% was demonstrated for fabricating 10-cm-diameter, 2.5-cm-thick TiC pieces. The CS/Ceracon-processed, high-density TiC specimen has a fine grain size, microhardness values exceeding 2,500 kg/mm ² , and compressive strength of 1.3 GPa. Due to the use of inexpensive conventional forging equipment and a low-cost grain for both initiating self-propagating, high-temperature synthesis (SHS) and consolidation, this novel approach has the potential to be significantly more cost effective than currently used conventional hot pressing (HP) or hot isostatic pressing (HIPing) of TiC and TiB ₂ powders. A set of recommendations for the technical approach to be followed in process upscaling in Phase II to fabricate larger size tiles of TiC material is provided.				
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